Underwater Adhesives/Attachments

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LONG-TERM GOALS

The long-term goal of the research is to expand mission capabilities of Naval Special Warfare (NSW) in the underwater attachment of munitions and sensor packages on a variety of surfaces, quickly, covertly, and under extreme environmental conditions.

OBJECTIVES

The objective of this program is to investigate new technologies for adhering and attaching to surfaces underwater in conditions found throughout the world. The state of current attaching technology presently limits mission capabilities because of duration of cure or complete ineffectiveness in cold seawater temperatures. The primary thrust of this effort is to overcome conventional attaching technology limitations in providing NSW the capability to complete attaching tasks unrestricted of seawater conditions.

APPROACH

This program has been executed in several phases leading up to the current pursuit of multiple parallel approaches for underwater bonding. While it has been the intent of this program to meet all requirements[1], overcoming the primary technical obstacle of bonding quickly even in cold temperatures has been the primary thrust. In FY97 industry was solicited for both commercially off-the-shelf

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **1998**	2. REPORT TYPE	3. DATES COVERED **00-00-1998 to 00-00-1998**
4. TITLE AND SUBTITLE **Underwater Adhesives/Attachments**		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Surface Warfare Center,Coastal Systems Station Dahlgren Division,6703 W. Highway 98,Panama City,FL,32407**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**		
13. SUPPLEMENTARY NOTES **See also ADM002252.**		
14. ABSTRACT		
15. SUBJECT TERMS		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**6**	

adhesives and proposals for developing new adhesive systems to meet NSW needs. No commercially available adhesives characterized or proposal evaluated were determined to meet NSW operational requirements. Multiple approaches have been pursued independently at the Naval Surface Warfare Center Dahlgren Division Coastal Systems Station (CSS), under contract with Dr. Brian Love, Dr. Wally Grant, and Mr. Carvel Holton of Virginia Polytechnic and State University (Virginia Tech), and under contract with Dr. James Crivello of Rensselaer Polytechnic Institute. As part of this program, the most appropriate technologies are to be identified for meeting operational requirements.

WORK COMPLETED

During the course of FY98, multiple technological approaches were pursued utilizing multiple sets of researchers in an attempt to increase the likelihood of success in identifying the most appropriate technology for meeting the requirements[1]. The requirements determination incorporated and consolidated several different mission operational requirements into one document. Although all requirements produced are considered important, the primary thrust of this research effort is overcoming attachment performance in cold seawater temperatures. Through the course of this program, it has become evident that fulfilling these requirements will greatly expand Special Operations Forces (SOF) opportunities.

Work completed has consisted of conducting feasibility studies on various technologies including redox-curable epoxy adhesives, thermally assisted conventional adhesives, multi-pore (suction cup) attachment methods, photo-curable methacrylate adhesives, and photo-curable epoxies. As a result of FY98 research, it has been concluded that the photo-curable methacrylate and epoxy technologies investigated will easily satisfy adhesive strength evolution requirements in low temperature conditions. Several successful adhesive formulations have been produced as part of the effort.

RESULTS

Redox Curable Epoxy Adhesives

Efforts to develop a redox curable epoxy that would cure rapidly in near freezing water were conducted by Rensselaer Polytechnic Institute and is documented in "Photo- and Redox Curable Epoxy Adhesives for Underwater Applications" [2]. The chemistry of the redox reaction is depicted below.

$$2\mathrm{Cu(II)L_2} + \mathrm{Sn(II)L_2} \longrightarrow 2\mathrm{Cu(I)L} + \mathrm{Sn(IV)L_4}$$

$$\mathrm{Cu(I)L} + \mathrm{Ar_2I^+X^-} \longrightarrow \mathrm{ArI} + [\mathrm{ArCu(III)LX}]$$

$$[\mathrm{ArCu(III)LX}] + \mathrm{M} \longrightarrow \mathrm{Ar\text{-}M^+X^-} + \mathrm{Cu(I)L}$$

$$\mathrm{Ar\text{-}M^+X^-} + \mathrm{NM} \longrightarrow \mathrm{Ar\text{-}(M)_nM^+X^-}$$

Despite the complex nature of this reaction, polymerizations are typically spontaneous, rapid and exothermic. Several formulations were developed in pursuit of a system that would satisfy the requirements. One such formulation is shown below.

Part A		Part B	
Vinylcyclohexene dioxide	2.4g	RG660 polyester	1.2g
IOC8 Initiator	0.5g	Coupling agent	0.3g
		Copper naphthenate	0.7g
		Stannous octoate	0.7g

In terms of reactivity, this system represents the highest attainable in a redox curable epoxy adhesive. When mixed at room temperature, the exotherm is so great that some of the monomer is vaporized. Underwater mixing produces steam. Attempts to cure the formulation in a 29° F water bath were made - the cure was observed to be very sluggish. Cure could only be obtained when a large mass of resin was present to provide sufficient exothermic heat to promote the reaction. Thin films of the adhesive would not cure in these cold water conditions. While the adhesive preformed well in ambient conditions, subsequent findings indicated a shelf-life stability issue with the copper catalyst. Over about a month period it was observed that the copper had reoxidized to form copper (II), which is inactive in the redox couple. Future efforts to formulate redox systems would need to address this stability issue. If the stability issue could be resolved, the redox system appears promising for in-air applications that require near-instant cure.

Thermally Assisted Conventional Adhesives

Virginia Tech investigated the potential of thermally assisted conventional adhesives to meet NSW requirements. The results of this effort are documented in “Energy Assisted Characterization of Marine Applications, Stage II - Heated Resin Feasibility Study” [3]. This effort was undertaken to determine whether it is feasible to heat commercially available adhesives in order to increase the reactivity of the adhesives to an acceptable level in near freezing seawater conditions. It was determined through modeling that thermal energy requirements are very much dependent on the substrate. Conductive substrates, such as steel (51.9 W/m- °C) and aluminum (200 W/m-°C) require an impractical amount of heat to increase the bond line reactivity to an acceptable level in near-freezing seawater conditions. Several exothermic chemical reactions were identified as candidates for possible future evaluation: AL/Fe Oxides and LiCl. In addition, experimentation was conducted by raising adhesive resin temperatures to a pre-set point (T_o) prior to submersion in water baths to determine the resulting conversion. Results indicated that the effects of the heat transfer to the surrounding water effectively terminated the reaction.

Photo-curable Methacrylate Adhesives

A photo-curable methacrylate, which would cure rapidly in near freezing water, was developed by Virginia Tech. This effort is documented in “Energy Assisted Adhesive Characterization for Marine Applications: Stage II - Light Curing Adhesive Feasibility Study” [4]. A methacrylate formulation was developed as part of this feasibility study (patent application is in process). The formulation utilizes camphorquinone as a light activated compound. The compound has a broad bad absorption with a maximum at a wavelength of approximately 470nm. The 470nm wavelength corresponds well with a blue LED that has been identified as a candidate irradiation source. Testing results to date indicate that the a single LED with adhesive will attach to substrates within two seconds at room temperature and five seconds in an ice bath. Additional efforts were made to produce an LED array for laboratory purposes that could be utilized to evaluate cure strength and cure rate of larger samples using LED's.

Testing to date has shown that at room temperature, 400 psi lap shear strengths using acrylic substrates can be produced within 30 seconds. Also, tensile tests of acrylic bonded to steel have shown results on the order of 200 psi within 30 seconds.

Photo-curable Epoxy Adhesives

A photo-curable epoxy which would cure rapidly in near freezing water was developed by Rensselaer Polytechnic Institute and is documented in “Photo- and Redox Curable Epoxy Adhesives for Underwater Applications” [2]. Several photo-curable epoxy formulations that are UV curable were developed as a part of this effort. A few are shown below.

Entry	**PC1000**	**Poly BD 605**	**ENR**	**SB Diblock**	**PBD Diol**	**Fume Silica**	**CHVE**	**DVE**	**Zonatac**
1	-	-	-	-	30	02	40	-	25
2	65	20	-	-	10	02	-	-	-
3	65	05	-	-	25	02	-	-	-
4	65	30	-	-	-	-	-	-	-

Note: All amounts are given in parts by weight. All formulations contained 3 wt % coupling agent and 2 wt % triethylenene glycol for vinyl ether formulations, and 5 wt % IOC 8 photoinitiator.

During the course of this study, cure was demonstrated to occur within 60 seconds in an ice bath using a laboratory UV irradiation source. Lap shear strengths have been demonstrated to be > 320psi.

Multipore Suction Technology

A nonadhesive multipore suction technology was investigated by CSS and is documented in “Multipore Suction Technology” [5]. As part of this effort, numerous types and sizes of suction cups were evaluated on surfaces of varying roughness and geometries (fouled marine surfaces were not evaluated) in order to determine the best performing geometry. The ridged-backed type cups with elastomeric seals outperformed all other types of cups evaluated. Although several failures were experienced, attachment using a single cup was accomplished underwater for 24 hours. A benchtop multi-cup static system was developed to illustrate ways of providing redundancy and increasing the reliability of the attachment. In addition to determining the best performing cups, it was found that the addition of a viscous fluid (such as petroleum product) between the elastomeric seal and the substrate improved the overall performance of the cups.

Actuation technologies for a multipore system were also investigated as a part of this effort. These technologies included Ti-Ni (muscle wire), solenoid, and pneumatic systems. After initial considerations of the above technologies, it was decided that due to time constraints that the focus would be primarily on demonstrating a pneumatic algorithm. A benchtop pneumatic system incorporating a limit switch was developed. The system is capable of sensing release and resetting. It is conceivable that a system such as this could be miniaturized and adapted to a multiple component actuation system.

IMPACT/APPLICATIONS

Overcoming conventional environmental constraints of underwater bonding will expand forward military opportunities in addition to providing direction for future system developments that require bonding, both topside and underwater. This technology could have immediate application for the attachment of explosives and shaped charges, markers, an underwater diver pad-eye or for limpet mines.

TRANSISTIONS

The technology is applicable to many Special Operations Forces (SOF) and Explosive Ordnance Disposal (EOD) mission scenarios. It is being transitioned for further development under shared funding from United States Special Operations Command and ONR's Surf Zone/Very Shallow Water (SZ/VSW) Mine Countermeasures (MCM) core program. It is expected to eventually transition to the VSW MCM Detachment in Coronado CA. Other fleet or commercial transitions are possible for applications that require quick bonding and attachment both in and above water.

RELATED PROJECTS

The Underwater Surface Preparation Technology Development Program begins in FY99. It will investigate/develop new technologies for preparing marine surfaces for adhesive bonding. Present attachment methods require at least minimal scraping that is unacceptable for some NSW applications.

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